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DEVELOPMENT OF SPACE STABLE THERMAL
CONTROL COATINGS FOR USE ON LARGE
SPACE VEHICLES

National Aeronautics and Space
Administration
George C. Marshall Space Flight Center
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FOREWORD


This is Report No. IITRI-C6233-52 (Triannual Report) of IITRI Project C6233, Contract No. NAS8-26791, entitled "Development of Space Stable Thermal Control Coatings for Use on Large Space Vehicles". This report covers the period from January 1 through April 30, 1975.

Major contributors to the program during this period include: Mr. J.E. Gilligan, Project Leader; Mr. Y. Harada and Mr. W. Logan, pigment manufacturing studies; Dr. C. Giori and Mr. T. Yamauchi, OI-650G preparation; Mr. F.O. Rogers, paint preparation; Messrs A. Lackland and J.E. Brzuskiwicz, irradiation experiments and reflectance measurements; and Dr. A.M. Stake, general consultation and administrative management.

The work reported herein was performed under the technical direction of the Space Sciences Laboratory of the George C. Marshall Space Flight Center; Mr. Daniel W. Gates acted as the Project Manager.

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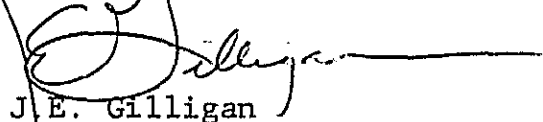


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TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	ii
1.0 INTRODUCTION	1
2.0 PIGMENT MANUFACTURING DEVELOPMENT STUDIES	2
2.1 Zinc Oxalate Studies	2
2.1.1 General	2
2.1.2 Preparation	3
2.1.3 Characterization Studies	5
2.1.3.1 Precipitation Yield	6
2.1.3.2 Phase Identification	6
2.1.3.3 SEM Studies	6
2.1.3.4 Calcination Studies	11
2.2 Stoichiometry Studies	11
2.2.1 Gravimetric Studies	16
2.2.2 SEM Studies	18
2.2.3 X-Ray Studies	18
2.2.4 Optical Spectra	27
3.0 IRRADIATION TESTING	33
4.0 REFERENCES	34

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
1	SUMMARY OF ZnOx PRECIPITATION STUDIES	4
2	SUMMARY OF STOICHIOMETRY STUDIES	17
3	IRIF-I-75 SAMPLE SCHEDULE	28

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1	SEM VIEWS OF ZINC OXALATE PRECIPITATES (ZnOx/RT and ZnOx/RT/60)	7
2	SEM VIEWS OF ZINC OXALATE PRECIPITATES (ZnOx/40/5 and ZnOx/40/60)	8
3	SEM VIEWS OF ZINC OXALATE PRECIPITATES (ZnOx/90/60 and ZnOx/RT/M-60)	9
4	SEM VIEWS OF ZINC OXALATE PRECIPITATES (ZnOx/55/M-5 and ZnOx/55/M-60)	10
5	SEM VIEWS OF ZINC OXALATE PRECIPITATES CALCINED AT 600°C (ZnOx/RT(6-2) and ZnOx/RT/60(6-2))	12
6	SEM VIEWS OF ZINC OXALATE PRECIPITATES CALCINED AT 600°C (ZnOx/40/5(6-2) and ZnOx/40/60(6-2))	13
7	SEM VIEWS OF ZINC OXALATE PRECIPITATES CALCINED AT 600°C (ZnOx/90/60(6-2) and ZnOx/RT/M-60(6-2))	14
8	SEM VIEWS OF ZINC OXALATE PRECIPITATES CALCINED AT 600°C (ZnOx/55/M-5(6-2) and ZnOx/55/M-60(6-2))	15
9	SEM VIEWS OF AS-MIXED OXALATES (Zn/Ti RATIO OF 1.90:1.00 and 1.95:1.00)	19
10	SEM VIEWS OF AS-MIXED OXALATES (Zn/Ti RATIO OF 2.00:1.00 AND 2.05:1.00)	20
11	SEM VIEWS OF MOX MATERIALS CALCINED AT 600°C (Zn/Ti RATIO OF 1.90:1.00 AND 1.95:1.00)	21

LIST OF FIGURES (Cont'd)

<u>Figure No.</u>		<u>Page</u>
12	SEM VIEWS OF MOX MATERIALS CALCINED AT 600°C (Zn/Ti RATIO OF 2.00:1.00 AND 2.05:1.00)	22
13	SEM VIEWS OF MOX MATERIALS CALCINED AT 900°C (Zn/Ti RATIO OF 1.90:1.00 AND 1.95:1.00)	23
14	SEM VIEWS OF MOX MATERIALS CALCINED AT 900°C (Zn/Ti RATIO OF 2.00:1.00 AND 2.05:1.00)	24
15	SEM VIEWS OF MOX MATERIALS CALCINED AT 1200°C (Zn/Ti RATIO OF 1.90:1.00 AND 1.95:1.00)	25
16	SEM VIEWS OF MOX MATERIALS CALCINED AT 1200°C (Zn/Ti RATIO OF 2.00:1.00 AND 2.05:1.00)	26
17	REFLECTANCE SPECTRA OF (6-9)Zn ₂ TiO ₄ PIGMENTS PREPARED AT VARIOUS Zn/Ti RATIOS	29
18	REFLECTANCE SPECTRA OF (6-12)Zn ₂ TiO ₄ PIGMENTS PREPARED AT VARIOUS Zn/Ti RATIOS	30

Report No. IITRI-C6233-52
(Triannual Report)

DEVELOPMENT OF SPACE STABLE THERMAL CONTROL
COATINGS FOR USE ON LARGE SPACE VEHICLES

1.0 INTRODUCTION

The effort in the research and development of passive spacecraft temperature control materials has, historically, concentrated on the development of the class of surfaces known as solar reflectors, surfaces with high reflectance for solar radiation and with high emittance in the thermal (infrared) spectrum. Basically, these surfaces must be optically stable in the total environment that they will experience. This requirement means that, once an high level of intrinsic stability in these materials is attained in the laboratory, we must make certain that this stability is preserved in a scaled-up process in manufacturing, that it is protected throughout the entire pre-launch environment, and, finally, that this stability obtains in the space environment. Applications on large space vehicles, therefore, present new R&D problems - not simply traditional ones in greater dimensions.

The program consists of four major tasks: pigment manufacturing development, binder development, environmental effects evaluations, and general coatings investigations. The relative emphasis on each of these tasks varies according to the urgency of the problems elucidated in our investigations, and, of course, with the availability of time and funds. Our present efforts have been expended primarily on the development of a mixed oxalate precursor zinc orthotitanate pigment manufacturing method and related studies and on complementary environmental testing and evaluation activities.

2.0 PIGMENT MANUFACTURING DEVELOPMENT STUDIES

Activities in this area were directed primarily at the improvement of the zinc oxalate precursor technique and in the elucidation of the effects of the Zn/Ti ratio on the optical spectra of zinc orthotitanate pigment. By precipitating the oxalates separately process conditions may be individually adjusted to attain desirable precipitate properties. While "TiOx" (the titanium precipitate in aqueous oxalic acid) possesses a fine particle size, ZnOx (its zinc analog) has a very large particle size. Our activities have thus been aimed at reducing the particle size of ZnOx. Also more work has been accomplished in determining the effects of varying the Zn/Ti ratio in the zinc orthotitanate precursor mixture. This effort is important in that it will establish realistic specifications on the mixing process in terms of both initial reflectance properties and optical stability in space applications.

2.1 Zinc Oxalate Studies

2.1.1 General

An effort has been initiated to establish a procedure for the production of a finer particle size zinc oxalate. A review of previous work with mixed oxalate (MOX) studies reveals the following:

- 1.) The reaction between ZnCl_2 and $\text{H}_2\text{C}_2\text{O}_4$ in aqueous solution at 90°C results in a precipitate of theoretical composition $(\text{Zn}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O})$ and yield.
- 2.) In earlier studies a one hour hold at 90°C was set as a standard precipitation condition for both zinc oxalate (ZnOx) and titanium "oxalate" ("TiOx"). Precipitation of the latter requires such a condition for complete reaction.

- 3.) The ZnOx precipitate obtained under these conditions is considerably coarser in particle size than the "TiOx". This was observed during filtration and confirmed in SEM examinations.
- 4.) Calcinations of "MOX" materials show that, with all other conditions the same, the particle size of the fired product, Zn_2TiO_4 , is directly related to the particle size of the precursor.

A finer particle size ZnOx is desirable from two standpoints: first, to obtain precursors of finer particle size and thus also of the fired product, and second, to obtain improved mixing of ZnOx with "TiOx". A closer match of the particle sizes of the ZnOx and TiOx should improve mixing and enhance the reactivity as well as the uniformity in the reacted binary oxide.

Experimental work was directed toward establishing the conditions necessary for obtaining ZnOx of a fine particle size. It was theorized that the fairly coarse size of ZnOx from a 90°C/1 hr precipitation could result from nucleation and growth afforded by the relatively high temperature-long time conditions. Accordingly, precipitations were carried out under lower temperatures and abbreviated times as shown in Table 1. Some of these experiments were also carried out in alcohol (rather than aqueous) media. Early work in coprecipitation had shown that an extremely fine particle morphology could be achieved in this way.

2.1.2 Preparation

The ZnCl_2 solutions were prepared by dissolving 50 grams of ZnCl_2 in 100 ml of H_2O or in 150 ml of CH_3OH . The reactions were observed to be exothermic. Oxalic acid solutions were prepared by dissolving 50 grams $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 350 ml H_2O or in 350 ml of CH_3OH . These dissolutions are endothermic. For experiments in ethanol and isopropanol media the amounts used were 25 grams ZnCl_2 in 100 ml of alcohol and 25 grams $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 200 ml of alcohol.

TABLE 1

SUMMARY OF ZnOx PRECIPITATION STUDIES

Sample *	Precipitation Conditions		Precipitate	
	Temp, °C	Medium	Particle Size, (μ)	Wt. Loss, % 600°C/2 hr
ZnOx/10/60	10	H ₂ O		56.97
ZnOx/RT**	room	H ₂ O	0.5-2	57.07
ZnOx/RT/60	room	H ₂ O	0.5-2	57.07
ZnOx/40/5	40	H ₂ O	0.5-3	57.06
ZnOx/40/60	40	H ₂ O	0.5-3	57.03
ZnOx/90/60	90	H ₂ O	1-4	57.03
ZnOx/RT/M-60	room	CH ₃ OH	0.2-1	57.07
ZnOx/55/M-5***	55	H ₂ O-CH ₃ OH	0.5-2	57.27
ZnOx/55/M-60***	55	H ₂ O-CH ₃ OH	0.5-2	57.55
ZnOx/RT/E-60	room	C ₂ H ₅ OH		56.23
ZnOx/RT/I-60	room	C ₃ H ₇ OH (2-propanol)		56.84

*Sample notation: ZnOx/Temperature (°C)/time of stirring in minutes at temperature.

**ZnCl₂ solution added to H₂C₂O₄ solution with no stirring. All other samples stirred for times shown.

***ZnCl₂ in H₂O + H₂C₂O₄ in CH₃OH.

The ZnCl_2 solution was reacted with the oxalic acid solution, with the latter being 10% in excess of the amount theoretically required to assure complete reaction. Precipitations in a water medium were observed to occur rapidly, resulting in rapid opacification of the liquid. On cessation of stirring, settling of the precipitate occurred within about 10 minutes, leaving a clear supernatant liquid.

Alcohol precipitations showed somewhat different characteristics. In a methanol system, the zinc oxalate appeared to form as very fine particles. This was evidenced in a translucent (as opposed to opaque) appearance of the liquid-solid system, and also by longer times for settling of the solids. In the cases of ethanol and iso-propanol, a gel-like precipitate formed rapidly upon addition of the reactants. The gelatinous nature of the precipitate caused it to remain in a suspended state in the ethanol or isopropanol with little settling.

The zinc oxalate was recovered by vacuum filtration using a Buchner funnel system. All precipitates formed in aqueous media filtered readily. Those materials formed in alcohol media, particularly the $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in methanol, all required re-filtrations of the filtrate in order to completely recover the solids. This is further evidence of the colloidal nature of these precipitates. All materials were washed thoroughly in water or alcohol (the wash medium was the same composition as the precipitation medium), until a neutral pH was achieved in the filtrate. The final step was air-drying in an oven at 80°C for 16 hours.

2.1.3 Characterization Studies

In characterizing the various precipitates, data were obtained on precipitation yield, phase identification (X-ray), particle morphology (SEM), and percentage weight loss on thermal decomposition to ZnO .

2.1.3.1 Precipitation Yield

The theoretical yield in the $\text{ZnCl}_2 + \text{H}_2\text{C}_2\text{O}_4$ reaction is calculated from a simple molecular weight relationship, i.e., 1 mol of ZnCl_2 or 136.28 grams will produce 1 mol of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ or 189.42 grams. As shown in Table 1, a 100% yield was obtained in all of the aqueous media precipitations, including the ice bath or 10°C experiment (ZnOx/10/60).

The use of an alcohol medium resulted in low yields (Table 1). Experiments were conducted to determine if $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ might be soluble in alcohol. The results showed no detectable solubility in methanol, ethanol, or isopropanol, ruling this out as a possible reason for the low yields. When left to stand, precipitates formed in these clear alcohol filtrates. This occurred within one hour in the isopropanol system, somewhat more slowly in the ethanol system, and very slowly (days) in the methanol system.

2.1.3.2 Phase Identification

Analysis of precipitates obtained in water and/or methanol media by X-ray techniques show them to be $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

2.1.3.3 SEM Studies

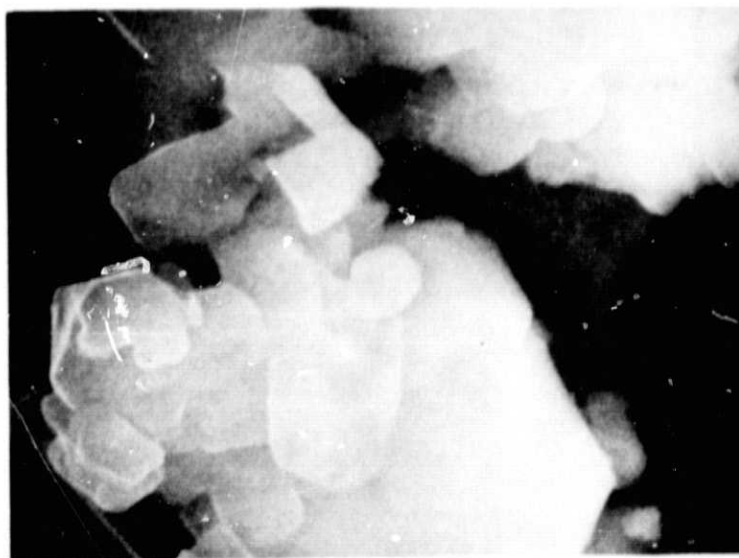
SEM photomicrographs (supplied through the courtesy of D.W. Gates) of various precipitates are presented in Figures 1 through 4. These show that precipitations conducted in water at moderate (room to 40°C) temperatures yield particles which are finer than that obtained at "standard," conditions i.e., ZnOx/90/60 (Figure 3). The finest precipitate was that obtained in a methanol medium at room temperature (ZnOx/RT/M-60 in Figure 3).



No. 624

ZnOx/RT

10KX



No. 623

ZnOx/RT/60

10KX

Figure 1. SEM Views of Zinc Oxalate Precipitates
(ZnOx/RT and ZnOx/RT/60)

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No. 628

ZnOx/40/5

10KX



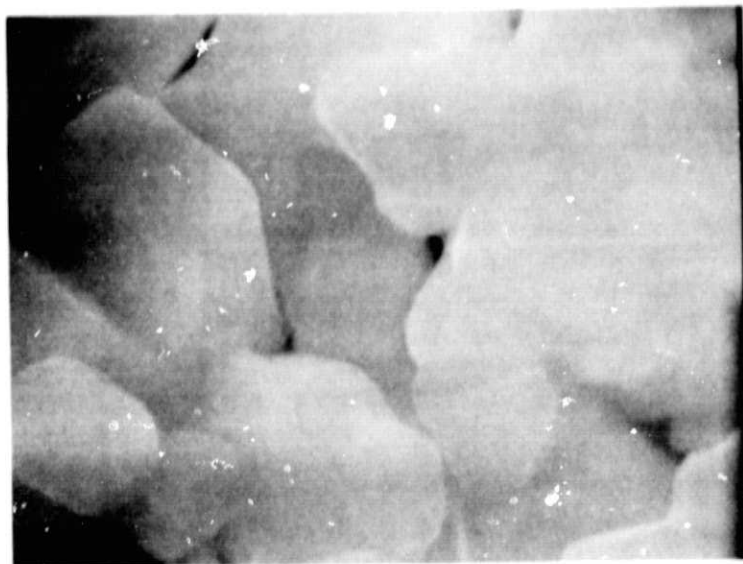
No. 629

ZnOx/40/60

10KX

Figure 2. SEM Views of Zinc Oxalate Precipitates
(ZnOx/40/5 and ZnOx/40/60)

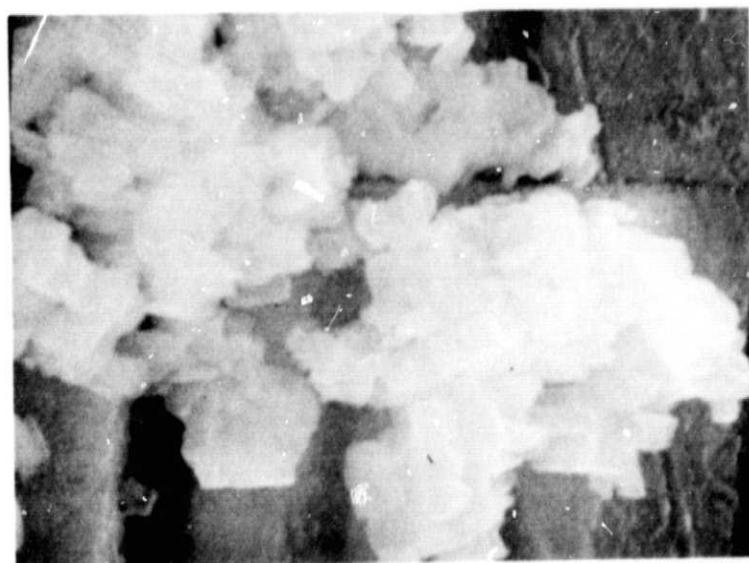
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No. 625

ZnOx/90/60

10KX



No. 631

ZnOx/RT/M-60

10KX

Figure 3. SEM Views of Zinc Oxalate Precipitates
(ZnOx/90/60 and ZnOx/RT/M-60)

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No. 627 ZnOx/55/M-5 10KX



No. 626 ZnOx/55/M-60 10KX

Figure 4. SEM Views of Zinc Oxalate Precipitates
(ZnOx/55/M-5 and ZnOx/55/M-60)

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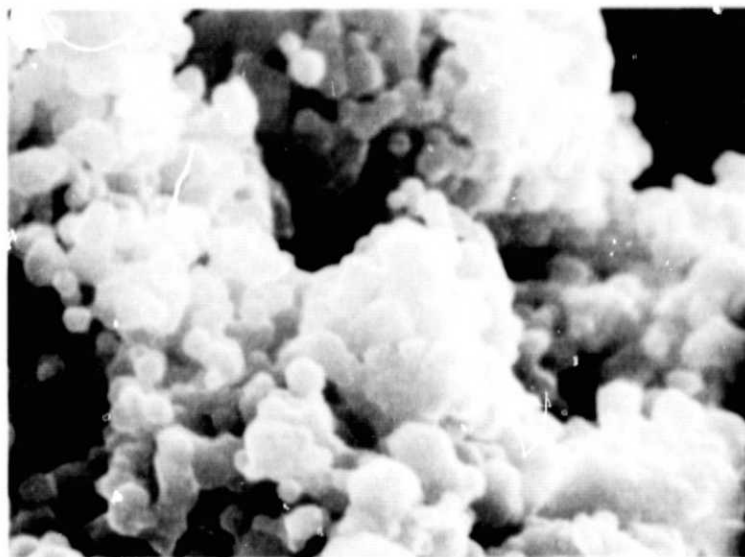
Photomicrographs of calcined (600°C/2 hrs) precursor materials, i.e., zinc oxide obtained by thermal decomposition of zinc oxalate, are presented in Figures 5 through 8. Among the precipitates, the methanol precipitate (ZnOx/RT/M-60) was clearly of finer particle size, and the "standard" precipitate (ZnOx/90/60) was considerably coarser than the other zinc oxalates. Among the calcined products, this size relationship no longer holds for the methanol material, but the calcined "standard" material is significantly coarser. The current materials all exhibit submicron particles with the largest size being about one micron.

2.1.3.4 Calcination Studies

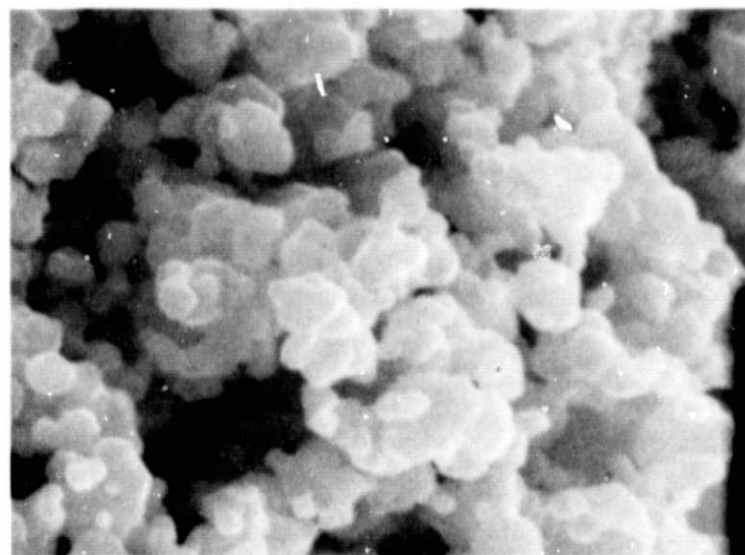
Percentage weight losses on decomposition of the oxalate precursor to ZnO by calcination at 600°C/2 hrs are also listed in Table 1. The theoretical weight loss for $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{ZnO}$ is 57.04%. As the data show, the experimental values are very close to the theoretical value for the water precipitated materials. The alcohol precipitated materials exhibited calcination weight losses which were not as close to the 57.04% value. Completion of SEM and X-ray evaluation of ethanol and isopropanol precipitates should help to explain this condition.

2.2 Stoichiometry Studies

Very definitive stoichiometry studies, in which reflectance properties are correlated in terms of Zn/Ti ratios (in the production of Zn_2TiO_4), have been carried out. The earlier assumption that a Zn/Ti ratio of 2.05:1.00, (i.e., an excess ZnO), is necessary for precluding free TiO_2 in Zn_2TiO_4 is invalid. In recent studies of a material with a Zn/Ti ratio of 1.5:1.0, both X-ray and spectral reflectance evaluations revealed no evidence of free TiO_2 . Therefore, it now appears that a closer approach to a 2.0:1.0 ratio of Zn/Ti may be desirable in that the "ZnO

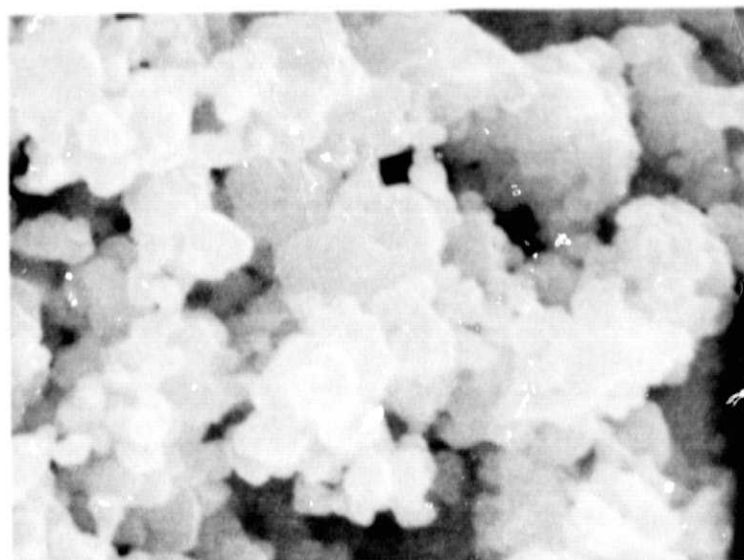


No. 641 ZnOx/RT(6-2) 10KX

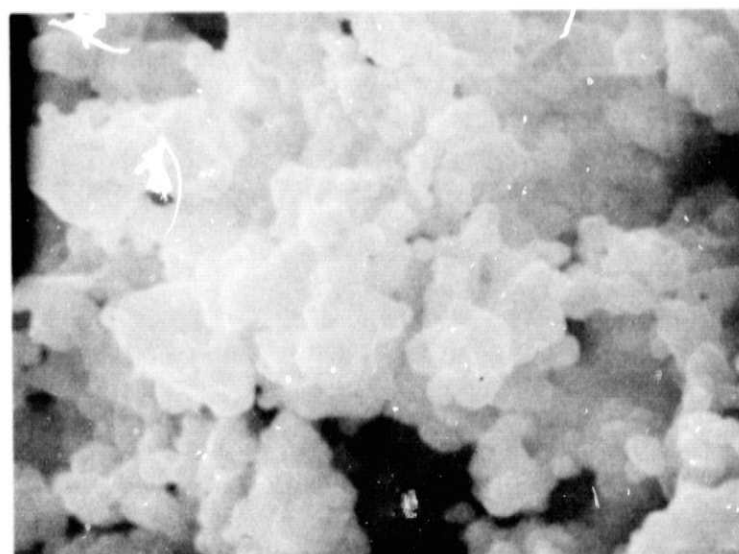


No. 644 ZnOx/RT/60(6-2) 10KX

Figure 5. SEM Views of Zinc Oxalate Precipitates
 Calcined at 600°C
 (ZnOx/RT(6-2) and ZnOx/RT/60(6-2))



No. 638 ZnOx/40/5(6-2) 10KX

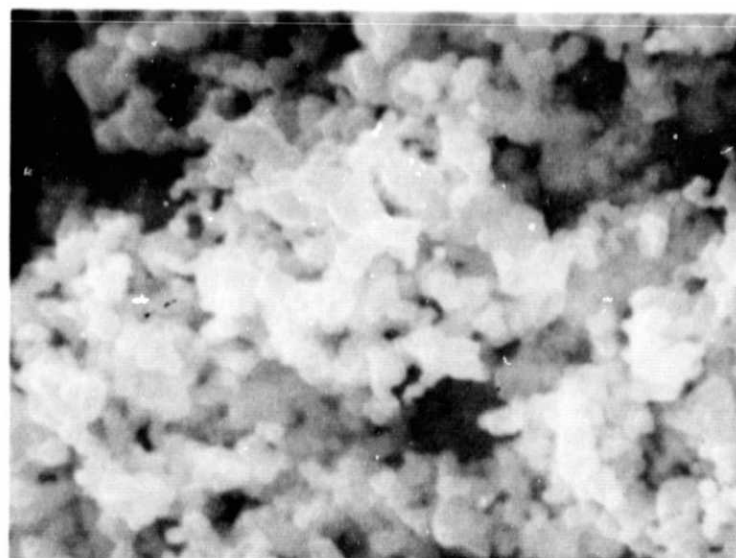


No. 645 ZnOx/40/60(6-2) 10KX

Figure 6. SEM Views of Zinc Oxalate Precipitates
 Calcined at 600°C
 (ZnOx/40/5(6-2) and ZnOx/40/60(6-2))

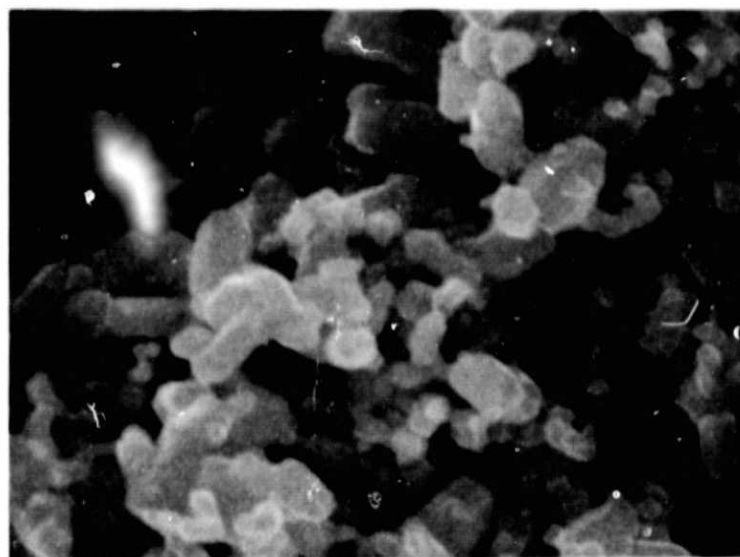


No. 643 ZnOx/90/60(6-2) 10KX

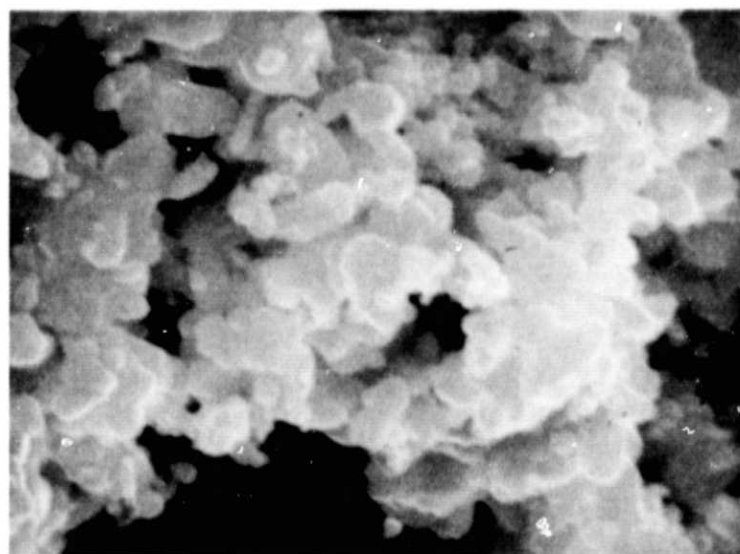


No. 642 ZnOx/RT/M-60(6-2) 10KX

Figure 7. SEM Views of Zinc Oxalate Precipitates
 Calcined at 600°C
 (ZnOx/90/60(6-2) and ZnOx/RT/M-60(6-2))



No. 640 ZnOx/55/M-5(6-2) 10KX



No. 639 ZnOx/55/M-60(6-2) 10KX

Figure 8. SEM Views of Zinc Oxalate Precipitates
 Calcined at 600°C
 (ZnOx/55/M-5(6-2) and ZnOx/55/M-60(6-2))

shoulder" in the absorption edge can be eliminated, thus resulting in a lower α_s pigment.

The present experiments were conducted with four Zn/Ti ratios: 1.90:1.00, 1.95:1.00; 2.00:1.00, and 2.05:1.00. Starting materials were "TiOx" precipitated under 90°C/1 hr conditions and zinc oxalate, 40°C/1 hr. Mixtures were ball milled dry for 16 hours using a 33% ball charge and a 50% total charge. Examination of materials after milling showed that some caking had occurred which could have resulted in poor mixing.

The appropriate data are shown in Table 2. All of the oxalate mixtures (of each of the above stoichiometries) were calcined at 600°C/2 hr. One half of the mixture was then calcined at 900°C/2 hr and the other at 1200°C/2 hr.

2.2.1 Gravimetric Studies

The weight losses for the various samples after a 600°C/2 hr calcination were somewhat lower than the theoretical values (Table 2). The theoretical values are calculated on the assumptions of a 57.04% loss in the reaction: $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{ZnO}$, and a 46.73% loss in the reaction "TiOx" $\xrightarrow{\Delta} \text{TiO}_2$. The increasing trend in weight loss with higher Zn/Ti ratio, both for the theoretical and actual data, is due to the greater weight loss for the zinc component (57.04% vs. 46.73%).

Very small weight losses occurred following the 900°C and the 1200°C calcinations. It can also be seen that the relationship of increasing weight loss with increasing Zn/Ti ratio holds at these higher temperatures. These losses may be due either to loss of absorbed water and/or completion of the decomposition/reaction process. The latter mechanism appears to be valid in view of the increasing weight loss versus the increasing Zn/Ti ratio relationship. Water adsorption differences due to stoichiometry changes are unlikely.

TABLE 2

SUMMARY OF STOICHIOMETRY STUDIES

Zn/Ti Ratio	Calcination		% Wt. Loss*		Particle Size Microns (SEM)
	Temp., °C	Time, Hrs	Actual	Theoretical	
1.90:1	-	-	-	-	1-5
	600	2	53.65	54.02	SM**
	900	2	0.31		SM-2
	1200	2	0.40		1-4
1.95:1	-	-	-	-	1-4
	600	2	53.73	54.07	SM
	900	2	0.32		SM-2
	1200	2	0.41		1-5
2.00:1	-	-	-	-	SM-4
	600	2	53.83	54.13	SM
	900	2	0.35		SM-2
	1200	2	0.43		1-5
2.05:1	-	-	-	-	SM-5
	600	2	53.86	54.18	SM
	900	2	0.35		SM-2
	1200	2	0.45		1-4

*% Weight loss is determined as 100 times initial mass less final mass divided by initial mass. Actual values at 900°C + 1200°C indicate percent weight loss in the precursor (i.e. 600°C) material. Theoretical weight loss is calculated based on molecular weights of precursors (ZnOx and "TiOx") and fired products (ZnO and TiO₂). (See Par. 2.2.1)

**SM- Submicron

2.2.2 SEM Studies

The particle sizes indicated by SEM photographs of as-mixed materials were fairly large (see Table 2 and Figures 9 and 10). This is most likely due to the zinc oxalate size of about 0.5-3 microns and also to some agglomeration which occurred during calcination.

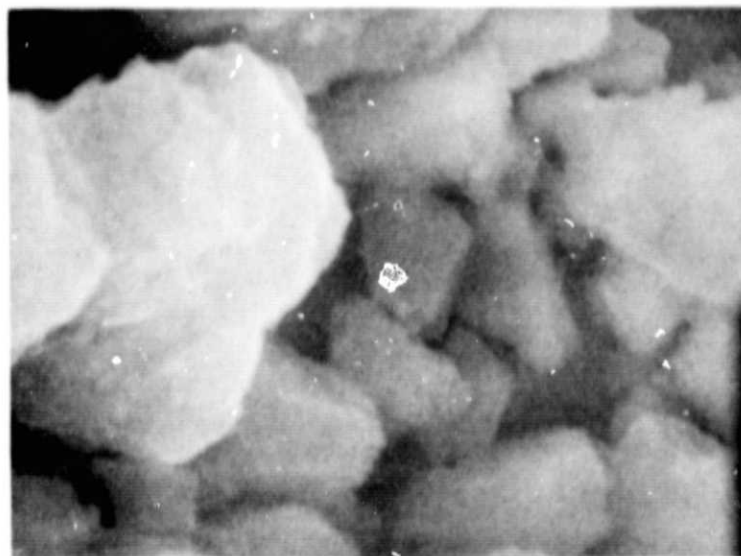
The materials after a 600°C/2 hr calcination were all extremely fine (submicron) in size, as shown in Figures 11 and 12. Such diminution in size from a coarser precursor can be expected when an oxalate (mixture) decomposes to the oxide with a substantial weight loss.

Calcination of the 600°C precursor at 900°C/2 hr and 1200°C/2 hr to obtain Zn_2TiO_4 resulted in coarser particles. Whereas a fairly high portion of the 900°C materials is submicron in size (Figures 13 and 14), the 1200°C calcination process apparently causes rapid growth of particles (Figures 15 and 16). As indicated in Table 2, no submicron particles exist in the samples calcined at high temperatures. From these experiments, it is apparent that a temperature lower than 1200°C is required to retain a population of submicron particles. This preliminary study, however, did not use optimized precursors, i.e., the finest particle size oxalates, and therefore, the particle size vs temperature data are not presented as conclusive.

2.2.3 X-Ray Studies

All of the stoichiometry samples were evaluated using X-ray analyses. Zinc orthotitanate was the major phase in all of the samples. The results can be summarized as follows:

1. 600°C calcination - Zn_2TiO_4 plus small amounts of ZnTiO_3 and ZnO . No evidence of TiO_2 .



No. 646 1.90:1.00 10KX



No. 661 1.95:1.00 10KX

Figure 9. SEM Views of As-Mixed Oxalates
(Zn/Ti Ratio of 1.90:1.00 and
1.95:1.00)

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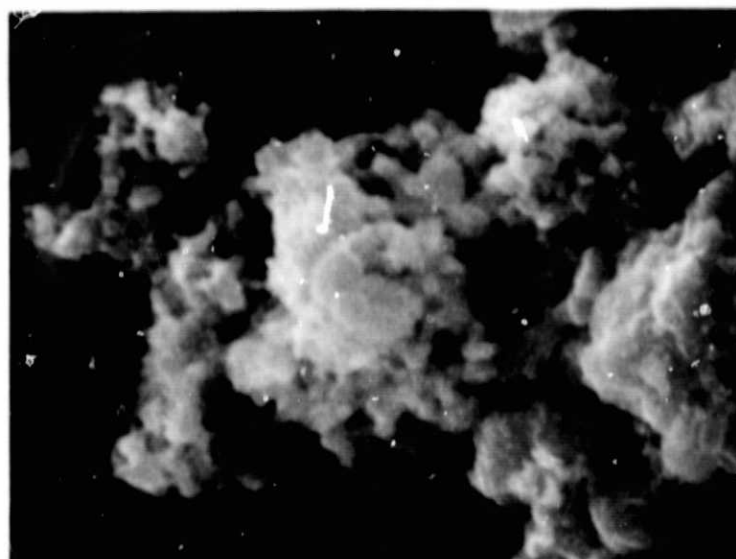
No. 662 2.00:1.00 10KX



No. 663 2.05:1.00 10KX

Figure 10. SEM Views of As-Mixed Oxalates
(Zn/Ti Ratio of 2.00:1.00 and
2.05:1.00)

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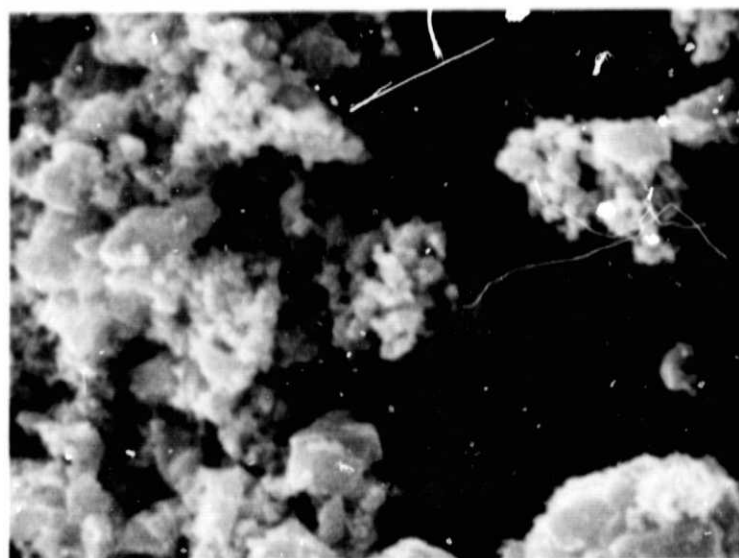


No. 647 1.90:1.00 10KX

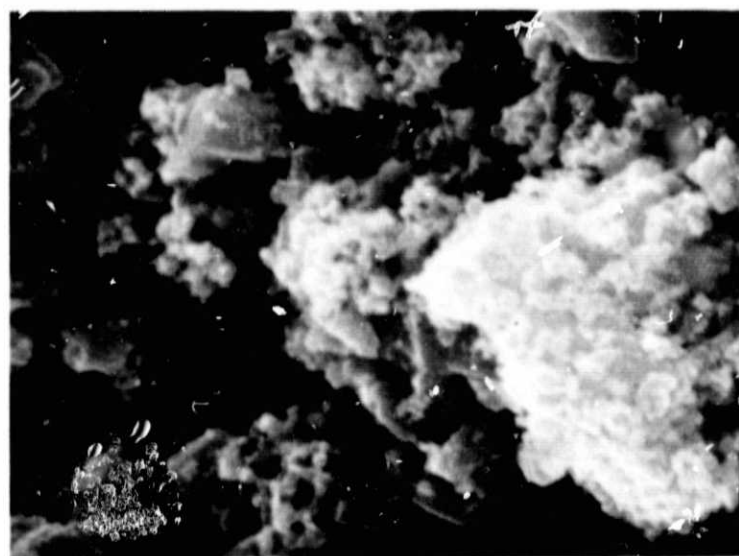


No. 658 1.95:1.00 10KX

Figure 11. SEM Views of MOX Materials Calcined at 600°C (Zn/Ti Ratio of 1.90:1.00 and 1.95:1.00)

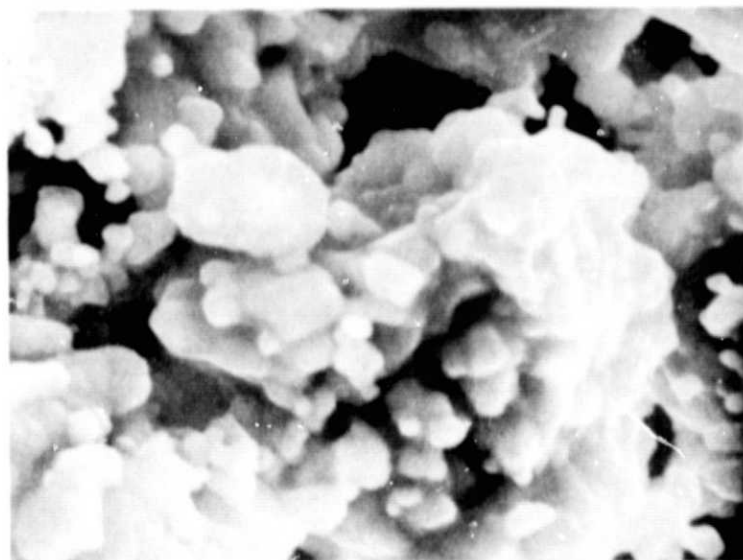


No. 659 2.00:1.00 10KX

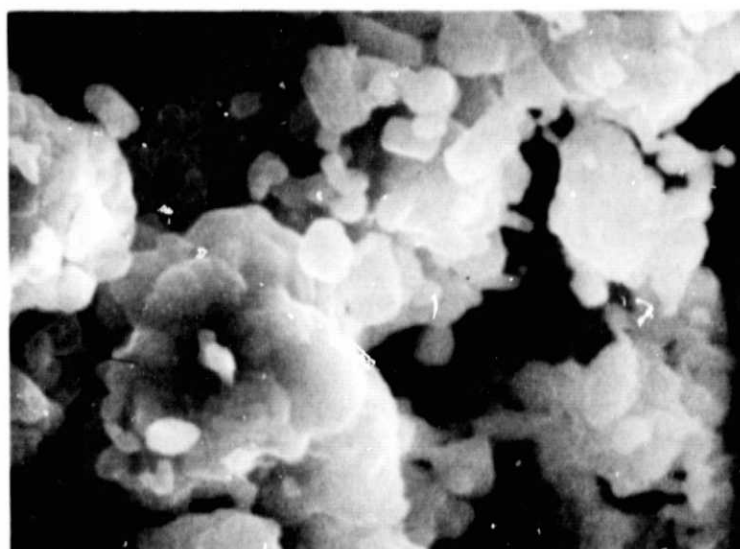


No. 660 2.05:1.00 10KX

Figure 12. SEM Views of MOX Materials Calcined at 600°C (Zn/Ti Ratio of 2.00:1.00 and 2.05:1.00)



No. 648 1.90:1.00 10KX

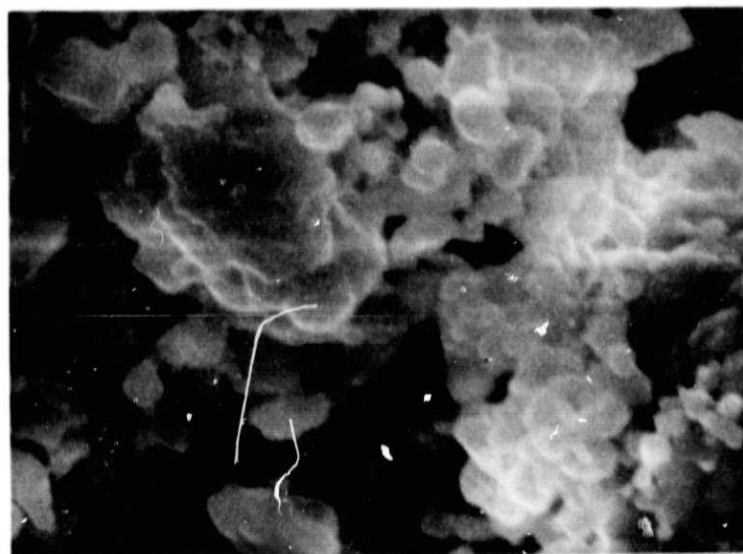


No. 652 1.95:1.00 10KX

Figure 13. SEM Views of MOX Materials Calcined at 900°C (Zn/Ti Ratio of 1.90:1.00 and 1.95:1.00)



No. 650 2.00:1.00 10KX



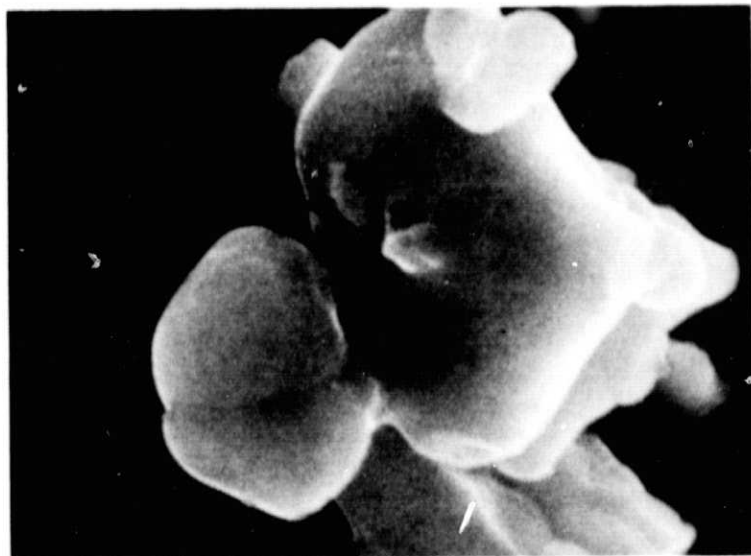
No. 651 2.05:1.00 10KX

Figure 14. SEM Views of MOX Materials Calcined at 900°C (Zn/Ti Ratio of 2.00:1.00 and 2.05:1.00)

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OF POOR QUALITY.

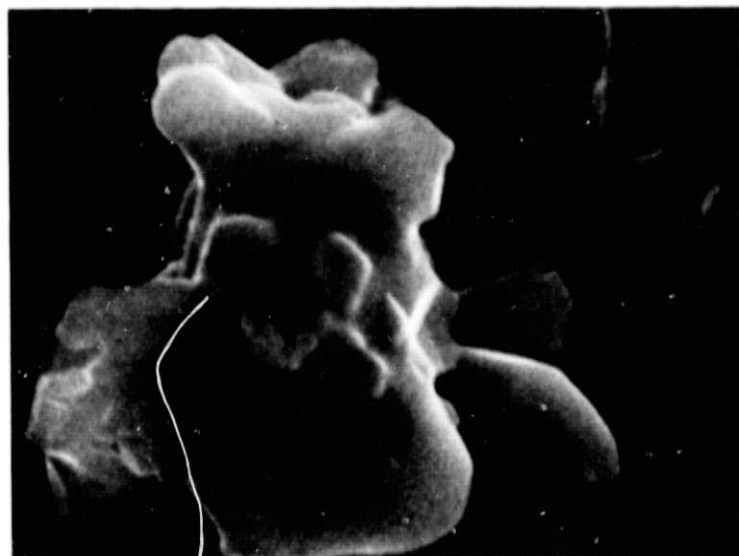


No. 649 1.90:1.00 10KX

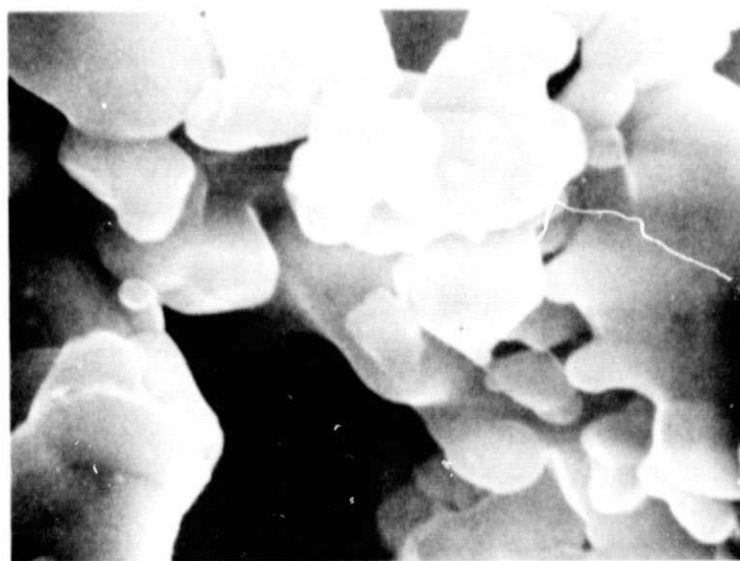


No. 655 1.95:1.00 10KX

Figure 15. SEM Views of MOX Materials Calcined at 1200°C (Zn/Ti Ratio of 1.90:1.00 and 1.95:1.00)



No. 653 2.00:1.00 10KX



No. 654 2.05:1.00 10KX

Figure 16. SEM Views of MOX Materials Calcined at 1200°C (Zn/Ti Ratio of 2.00:1.00 and 2.05:1.00)

2. 900°C calcination - Zn_2TiO_4 . Very faint evidence of ZnO in 2.00:1.00 and 2.05:1.00 Zn/Ti samples, estimated to be less than 4%. No other phases.

3. 1200°C - Same as 900°C.

2.2.4 Optical Spectra

The pigment powders described previously were deposited on IRIF sample coupons from water slurries. After the samples were dried, their diffuse reflectance spectra were measured in the spectral region from 325nm to 2600nm. As with previous experiments of this type, the spectra in the region from 500 to 2600nm are not particularly significant (Ref. 1). Thus, we have omitted them from the spectra shown in Figure's 17 and 18. In Figure 17 are presented the spectra for samples of various Zn/Ti ratios which had been subjected to the "6-9" thermal treatment. Reflectance spectra of samples treated under "6-12" calcination conditions are presented in Figure 18. The trend in both cases is clear and consistent. As the Zn/Ti ratio increases the tendency to form ZnO increases also.

Other significant observations are that the spectra of materials with Zn/Ti ratios of 1.90 and 1.95 do not differ substantially. In Table 3 we have listed some of the reflectance properties and extinction coefficients derived from them (according to the procedures developed and explained in Ref. 1). Note in Table 3 that the 6-9 materials have very much less K_{350} values at Zn/Ti ratios of 1.90 and 1.95 than do those for 6-12 materials. Comparing the spectra of 6-9 materials directly with those of the 6-12 materials discloses a substantial difference between their effective band gap energies (i.e. E_g); 6-9 materials have a larger band gap and the nature of their spectra suggests that

TABLE 3

IRIF-1-75[±] SAMPLE SCHEDULE:
 SERIES OF Zn_2TiO_4 PIGMENTS WITH DIFFERING Zn/Ti RATIOS

Sample No.	Sample Description**	R_{350}	R_{370}	R_{400}	R_{450}	R_{700}	R_{2600}	λ_{Max}	R_{i-r}	Coating Wt.	K_{350}	K_{450}	K_{i-r}
1	1.90 (6-9)	69.0	74.0	77.9	79.5	82.0	92.0	(2.6)	87	.0440	.3263	17.69	24.15
2	1.95 (6-9)	71.5	78.6	85.6	88.0	91.0	95.1	(2.6)	93	.0780	.2725	14.50	21.64
3	2.0 (6-9)	50.2	61.0	84.1	87.8	91.0	94.0	(2.6)	93	.0780	4.265	14.44	21.64
4	2.05 (6-9)	35.5	42.0	70.6	83.6	88.0	92.0	(2.6)	89	.0510	13.33	18.23	23.60
5	1.90 (6-12)	67.2	77.0	82.0	83.9	86.0	94.0	(2.6)	90	.0650	6.500	14.35	19.77
6	1.95 (6-12)	67.0	76.0	82.3	84.7	86.0	92.1	(2.6)	89	.0665	6.610	14.52	18.10
7	2.0 (6-12)	47.1	53.9	77.1	84.1	86.8	91.0	(2.6)	88	.0750	5.280	15.08	12.52
8	2.05 (6-12)	36.1	46.1	76.0	83.2	86.2	91.0	(2.6)	88	.0550	12.05	16.43	20.55
9	2.00 (6-9)Alc**29.9	42.0	42.0	75.1	78.8	82.2	83.5	(2.6)	87	.1500	5.665	5.12	7.55

*Samples were not irradiated

**All Descriptions indicates Zn/Ti ratio and heat treatment schedule; 1.90 (6-9) refers to a pigment prepared from a mixture of oxalates with a 1.90:1.0 Zn/Ti ratio calcined at 600°C for 2 hrs and again at 900°C for 2 hrs.

***All samples prepared by an aqueous "MOX" process, except #9 which was prepared from Alcohol solution of $H_2C_2O_4$

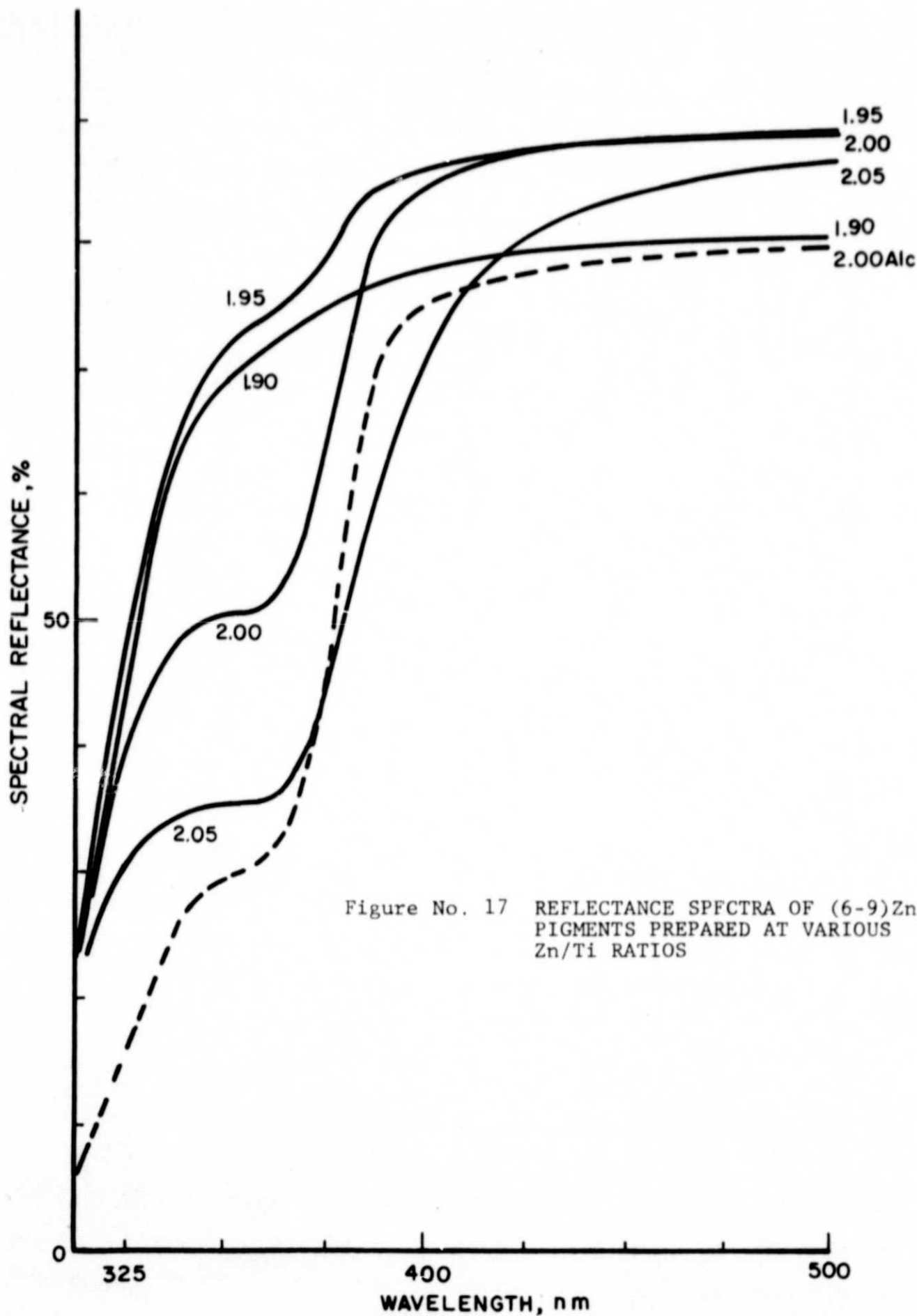


Figure No. 17 REFLECTANCE SPECTRA OF $(6-9)\text{Zn}_2\text{TiO}_4$ PIGMENTS PREPARED AT VARIOUS Zn/Ti RATIOS

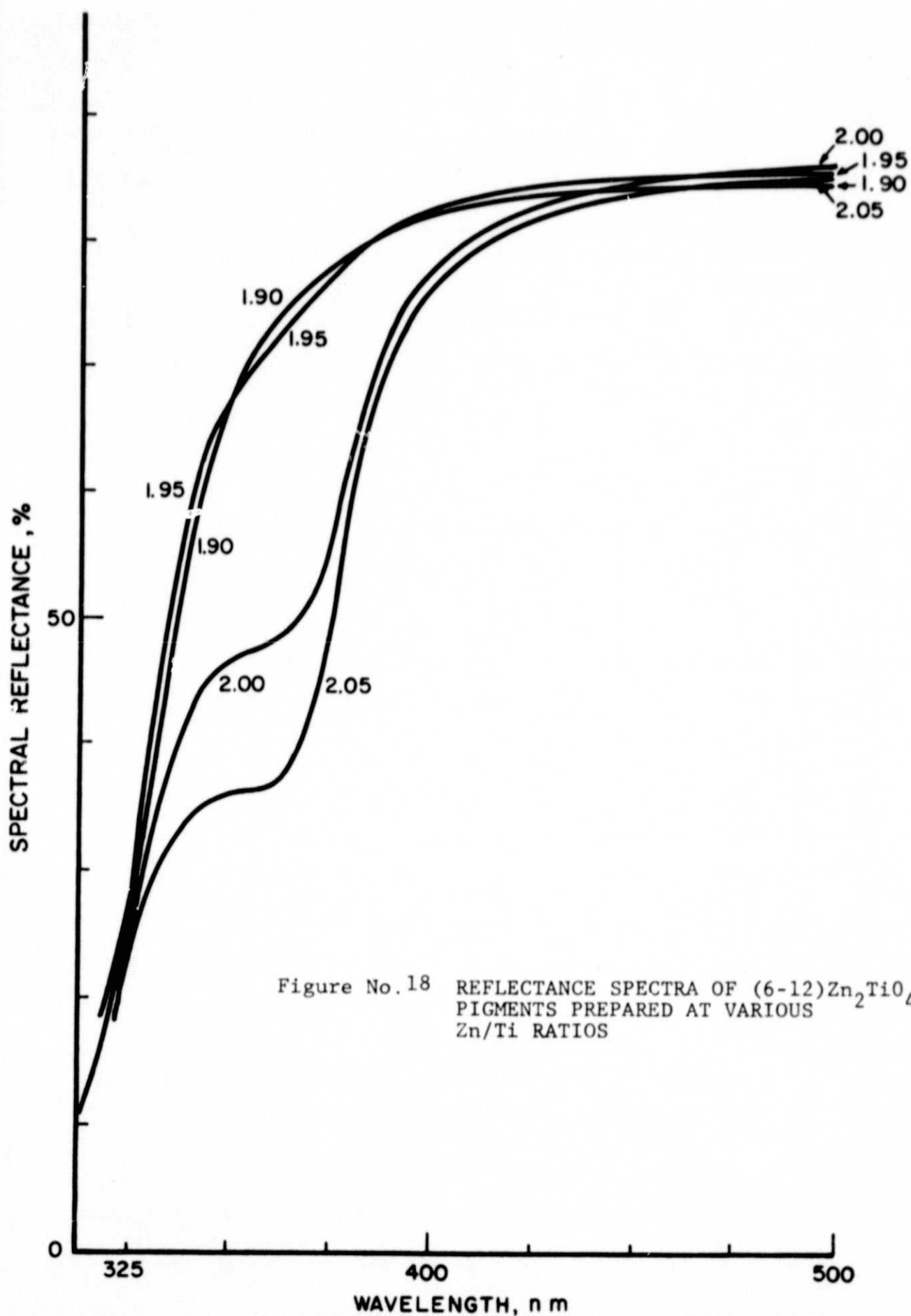


Figure No. 18 REFLECTANCE SPECTRA OF $(6-12)\text{Zn}_2\text{TiO}_4$
PIGMENTS PREPARED AT VARIOUS
Zn/Ti RATIOS

higher temperatures lead to different compounds (possibly sesqui-titanates) whose absorption in the 325-350nm region is noticeably higher than that for zinc orthotitanate.

The design of this experiment anticipated one of the effects which evidences itself in the trend of effective E_g with Zn/Ti ratio. The spectra show characteristic ZnO absorption at a Zn/Ti ratio of 2.0 and especially at 2.05 - in both the 6-9 and 6-12 materials. In preparing these materials the ZnOx material is assumed to be $ZnC_2O_4 \cdot 2H_2O$ with a molecular weight of 189.432. The molecular weight of "TiOx" is taken to be 150.00, based on gravimetric studies of the thermal conversion of "TiOx" to TiO_2 . The spectra reveal very definite evidence of ZnO at Zn/Ti ratios of 2.0 and 2.05. While we would expect this at 2.05, the finding of a significant amount of ZnO at 2.0 implies that the effective Zn/Ti ratio is greater than 2.0, and that, if we have complete confidence in the ZnOx mol. weight, the molecular weight of "TiOx" must therefore be greater than 150. This, of course is consistent with our earlier finding that "TiOx" is $Ti(OH)_2CO_3 \cdot 0.5H_2O$ (whose mol. wt. is 150.934). This conclusion assumes also, however, that the titanium components were not preferentially retained in mixing equipment or otherwise selectively removed from the zinc-titanium mixture in the process of preparing the various samples.

The intense absorption of ZnO below 360nm ($>10^6 \text{ cm}^{-1}$) would suggest that very small amounts (of the order of several tens of ppm) would be necessary to cause a significant reduction in the reflectance in the 325 - 360nm region. In other words the reflectance in this region can be expected to be highly sensitive to the concentration of ZnO.

Another comparison which may be made is that between sample No. 9 and the others. Sample No. 9 was prepared from oxalate precursors which had been precipitated in alcohol solutions (as opposed to aqueous solutions which are normally used). The spectra are shown in Figure 17 and the appropriate data have been listed in Table 3. Note that the properties of the alcohol sample differ markedly from those of the aqueous samples. The nature and shape of the spectra are indicative of a large particle size, larger than those of the aqueous materials. The shape of the reflectance spectrum below 400nm is also very interesting. The sharper absorption in the 376nm region suggests that the material has much more ZnO in it than an equivalent material prepared by aqueous precipitation.

3.0 IRRADIATION TESTING

The irradiation in IRIF-I-74 of Zn_2TiO_4 pigments treated with various chemical agents by Stanford Research Institute (SRI) (and also of OI-650G paints made from them) was completed. Reflectance spectra in the spectral range 325-2600nm were made prior to irradiation, after ultraviolet exposures of 100 ESH, 500 ESH, 1000 ESH and 1150 ESH, and finally after exposure to 760 torr O_2 . The spectra have been delivered to NASA-MSFC for transmittal to and evaluation by SRI.

4.0 REFERENCES

1. J.E. Gilligan and Y. Harada, "Development of Space Stable Thermal Control Coatings for Use on Large Space Vehicles;. IITRI Triannual Report C6233-48, Appendix I, February, 1975.